

## OSMIUM ALKYL COMPLEXES

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### A. INTRODUCTION

Over the past few years there have been a number of reviews devoted to compounds containing transition metal to carbon  $\sigma$ -bonds [1–4], and also on the formation and structure of transition metal-carbenes and -carbynes [5,6]. Very rarely, however, have reviews covered compounds containing osmium to carbon  $\sigma$ -bonds. This survey deals with the formation and structure of such osmium compounds and covers published literature up to the end of March, 1981; it excludes those compounds containing solely carbon monoxide groups and other simple carbon-containing ligands (e.g., thiocarbonyl and isocyanide ligands).

### B. MONO-NUCLEAR OSMIUM COMPLEXES

One of the first compounds thought to contain osmium–carbon  $\sigma$ -bonds was isolated in 1959 as a by-product in a study of complex hydrides. This product,  $\text{OsHCl}[\text{C}_2\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2$ , was characterised by infrared only [7].

The first well characterised complexes were made by the interaction of alkyl- and aryl-lithium compounds, and of neat trialkylaluminium on the dihalocomplexes, *cis*- and *trans*- $\text{OsCl}_2(\text{diphosphine})_2$ , (diphosphine =

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  or  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) [8]. The compounds prepared,  $\text{OsL}_1\text{L}_2(\text{diphosphine})_2$ , ( $\text{L}_1 = \text{Cl}$ ,  $\text{L}_2 = \text{Me}$  or  $\text{Et}$ ;  $\text{L}_1\text{L}_2 = \text{Me}_2$  or  $\text{Ph}_2$ , diphosphine =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), could be reduced by  $\text{LiAlH}_4$  to produce hydrido-alkyl or -aryl complexes.

The reduction of  $\text{OsH}_2(\text{CO})_4$  with sodium sand in tetrahydrofuran leads to the formation of  $\text{Na}[\text{OsH}(\text{CO})_4]$ , this can be treated with methyl-halides to yield the alkyl compounds,  $\text{OsH}(\text{CO})_4(\text{CH}_3)$ ,  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{I}$  and  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ ; which have been assigned *cis* stereochemistry by IR and NMR [2,9]. The reduction of  $\text{Os}_3(\text{CO})_{12}$  with Na in liquid ammonia and subsequent reaction with stoichiometric amounts of  $\text{MeI}$  also produces the same products [10].  $\text{Os}(\text{CO})_4(\text{CH}_2\text{CH}_3)_2$  is also prepared by similar reactions [11]. This complex reacts with bromine to produce  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{Br}_2$  and with carbon monoxide to yield  $\text{Os}(\text{CO})_4(\text{COC}_2\text{H}_5)_2$ . However, bromine only displaces one *n*-ethyl group from  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  to produce  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{Br}$ , but under carbon monoxide and elevated temperature the dimethyl complex is converted to  $\text{Os}(\text{CO})_5$  and ethane.

The reaction between methylfluorosulphonate and  $\text{Na}_2\text{Os}(\text{CO})_4$  produces  $\text{OsH}(\text{CO})_4\text{CH}_3$  in 97% purity [12] (contaminated with 3%  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ ).

$\text{Os}(\text{CO})_4(\text{CH}_3)_2$  and  $\text{Os}(\text{CO})_4(\text{C}_2\text{H}_5)_2$  do not decompose appreciably below  $100^\circ\text{C}$  [13], whereas  $\text{OsH}(\text{CO})_4(\text{CH}_3)$  decomposes rapidly at  $40^\circ\text{C}$ .

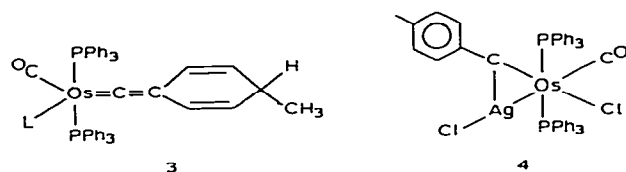
$\text{Os}(\text{CO})_4(\text{CH}_3)_2$  decomposes by metal-carbon bond homolysis to form free radicals [13]. The methyl radicals produced (slowly even at  $163^\circ\text{C}$ ) attack a wide variety of solvents, producing mainly methane. An excess pressure of methane has no significant effect on the rate of decomposition [14].

Carbon-13 variable temperature NMR techniques [15] have shown that the methyl-carbon atoms in  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  relax by both dipolar and spin-rotation mechanisms.

The reaction between  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HgR}_2$  ( $\text{R} = p\text{-tolyl}$ ) in toluene, deposits mercury and yields a red solution from which crystals of  $\text{OsRCl}(\text{CO})(\text{PPh}_3)_2$  can be isolated in 95% yield [16]. Other halo-derivatives can be prepared by reacting  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  with  $\text{AgClO}_4$  followed by  $\text{NaX}$ . These products rapidly react with CO to yield  $\text{OsRX}(\text{CO})_2(\text{PPh}_3)_2$  which is non-reversible, unlike the ruthenium analogue.

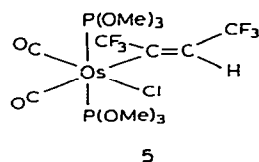
The cations  $[\text{Os}(\text{CR})(\text{CO})_2(\text{PPh}_3)_2]^+$  (1) and  $[\text{Os}(\text{CR})(\text{CO})-(\text{CNR})(\text{PPh}_3)_2]^+$  (2) have been prepared from the reaction of  $\text{AgClO}_4$  with  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , ( $\text{R} = p\text{-tolyl}$ ), in the presence of CO or CNR respectively [17]. Addition of  $\text{Li}(\text{Et}_3\text{BH})$  to either (1) or (2) leads to the production of vinylidene complexes (3), whose structure has been confirmed by X-ray spectroscopy.

$\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  also reacts with Group Ib halides to form mixed dimetallocyclopropene species  $\text{Os}(\text{X})(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , (4) ( $\text{X} = \text{CuI}$ ,



AgCl, AuCl) [18]. Crystal structure analysis shows the presence of a 3-membered ring in which the Os–C  $\sigma$ -bond length has increased from 1.77 to 1.84 Å due to coordination of AgCl.

Reaction of hexafluorobut-2-yne with *trans*-Os(CO)<sub>3</sub>[P(OMe)<sub>3</sub>]<sub>2</sub> yields hexafluorobut-2-yne-*cis*-dicarbonyl-*trans*-bis(trimethylphosphite)osmium [19], which, when reacted with HCl in hexane yields complex (5).



The reactions of OsH(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> and Os(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with acetylenes also leads to the formation of Os–C  $\sigma$ -bonds [20]. Diphenylacetylene inserts into the metal–hydrogen bond to form Os{C(Ph)=CHPh}(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>. Phenylmethylacetylene likewise inserts but gives a 1:1 mixture of Os{C(Ph)=CHMe}(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> and Os{C(Me)=CHPh}(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, presumably implying that the stereochemistry of insertion is governed by a delicate balance of steric and electronic factors.

The first example of a dichlorocarbene complex, OsCl<sub>2</sub>(CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> [21] was produced by the reaction of OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> with Hg(CCl<sub>3</sub>)<sub>2</sub> in 80% yield. Carbon-13 NMR shows the carbene carbon resonating at 223.2 ppm (CDCl<sub>3</sub>, SiMe<sub>4</sub>).

The reaction of the dichlorocarbene complex OsCl<sub>2</sub>(CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> with lithium reagents, LiR, produces the carbyne complex OsCl<sub>2</sub>(CR)(CO)(PPh<sub>3</sub>)<sub>2</sub> [22], which contain an osmium–carbon bond with length 1.77 Å, and having  $\nu$ (OsC) at 1358 cm<sup>–1</sup>. With HX, OsCl<sub>2</sub>(CHR)(CO)(PPh<sub>3</sub>)<sub>2</sub>, and with Cl<sub>2</sub>, OsCl<sub>2</sub>(CClR)(CO)(PPh<sub>3</sub>)<sub>2</sub>, are produced.

The reaction of Os(C<sub>2</sub>H<sub>4</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with CS<sub>2</sub> yields Os(CS<sub>2</sub>)-(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [23], and this rapidly reacts with methyl iodide to form the cation [Os(CS<sub>2</sub>Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in which the CS<sub>2</sub>Me group bonds through a carbon and one sulphur atom. If excess methyl iodide is used then the dithiocarbene complex [OsI{C(SMe)<sub>2</sub>}(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> is produced.

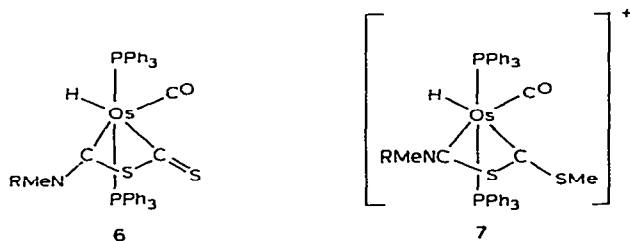
The osmium cation [Os(CS<sub>2</sub>Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> reacts with NaBH<sub>4</sub> to

produce  $\text{OsH}(\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  [24]. Infrared studies show that this includes the monodentate dithiomethylester ligand. On refluxing in 2-methoxyethanol, methylthiol is eliminated and the zerovalent complex  $\text{Os}(\text{CS})(\text{CO})_2(\text{PPh}_3)_2$  results. In benzene this latter product reacts with  $\text{CS}_2$  to produce  $\text{Os}(\text{CS}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$  [25]. This can be rapidly methylated by  $\text{CF}_3\text{SO}_3\text{CH}_3$  to yield  $[\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ . If this is reacted with aqueous  $\text{HX}$  under reflux then  $\text{OsX}_2(\text{CS})_2(\text{PPh}_3)_2$  is produced.

The reaction of  $\text{Os}(\text{CS}_2)(\text{CO})_2(\text{PPh}_3)_2$  with 1,2-dibromoethane and subsequent addition of  $\text{NaClO}_4$  produces the cyclic carbene compound  $[\text{OsBr}(\overline{\text{C}}\text{SCH}_2\text{CH}_2\text{S})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ , which has been characterised by  $^1\text{H}$  NMR and IR [26].  $\text{Os}(\text{CS}_2)(\text{CO})(\text{CNR})(\text{PPh}_3)_2$  also reacts similarly and the carbene compound  $[\text{OsCl}(\overline{\text{C}}\text{OCH}_2\text{CH}_2\text{O})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]\text{ClO}_4$  has been identified by  $^1\text{H}$  NMR.

The reaction between  $[\text{OsCl}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]^+$  and  $\text{SH}^-$  leads to a mixture of  $\text{Os}(\eta^2\text{-SCNR})(\text{CS})(\text{CO})(\text{PPh}_3)_2$  and  $\text{Os}(\eta^2\text{-CS}_2)(\text{CO})(\text{CNR})(\text{PPh}_3)_2$  [27]. When the same cation is treated with  $\text{SeH}^-$  the exclusive product is  $\text{Os}(\eta^2\text{-CSeS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2$ . Reacting this product with  $\text{MeI}$  a dihapto-methylselenothioester complex is produced. With  $\text{HCl}$ , the product is  $[\text{OsCl}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]^+$ ; and with  $\text{NaBH}_4$  a zerovalent thio-carbonyl complex is produced,  $\text{Os}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2$ .

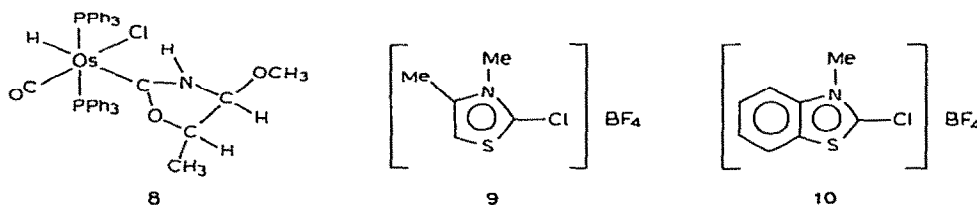
The reaction of  $[\text{Os}(\eta^2\text{-SCNMeR})(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+$  with  $\text{NaBH}_4$  leads to the formation of  $\text{Os}(\text{CS}_2\text{CNMeR})\text{H}(\text{CO})(\text{PPh}_3)_2$  (6) [28] which contains a 4-membered metallocycle. The *exo*-sulphur atom can be methylated by reaction with methyl iodide to form  $[\text{Os}\{\text{C}(\text{SMe})\text{SCNMeR}\}\text{H}(\text{CO})(\text{PPh}_3)_2]^+$  (7) in which the ligand is formally a bidentate dicarbene.



Transfer rearrangement [29,30] occurs when  $\text{OsHX}(\text{CS})\text{L}(\text{PPh}_3)_2$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{L} = \text{CO}$ ;  $\text{X} = \text{Cl}, \text{L} = \text{CN-}p\text{-tol}$ ), containing *cis*-hydrido and thio-carbonyl ligands, is treated with carbon monoxide in benzene at room temperature to form  $\text{OsCl}(\text{CHS})(\text{CO})_2(\text{PPh}_3)_2$ . Similarly, the complexes  $\text{OsRX}(\text{CS})\text{L}(\text{PPh}_3)_2$ , ( $\text{R} = p\text{-tol}, \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{O}_2\text{CCF}_3, \text{L} = \text{CO}$  or  $\text{CNR}$ ), with adjacent  $\text{R}$  and  $\text{CS}$  ligands also rearrange [31] (on refluxing with  $\text{HgR}_2$  in toluene) to form dihapto-thioacyl complexes  $\text{Os}(\eta^2\text{-C}\{\text{S}\}\text{R})\text{XL}(\text{PPh}_3)_2$ , and their formulation has been confirmed by X-ray structural determination.

Tosylmethylisocyanide (TMIC) reacts with  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  to yield

$\text{OsHCl}(\text{CO})(\text{TMIC})(\text{PPh}_3)_2$  which, when further reacted with  $\text{CH}_3\text{CHO}$  and  $\text{NaOCH}_3$ , produces the cyclic carbene complex (8) [32].

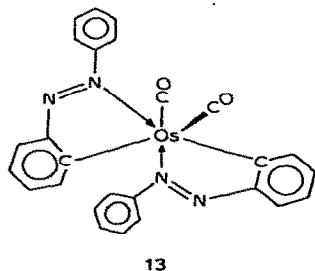


The anion obtained from the reaction of dodecacarbonyltriosmium with sodium in liquid ammonia reacts with the salts (9) and (10), to produce  $\text{Os}(\text{CO})_4[\text{CN}(\text{Me})\text{C}(\text{Me})\text{CHS}]$  (11) and  $\text{Os}(\text{CO})_4[\text{CN}(\text{Me}) \cdot \text{C}_6\text{H}_4 \cdot \text{S}]$  (12) respectively [33]. Simple substitution of (11) occurs with  $\text{Ph}_3\text{P}$  to give  $\text{Os}(\text{CO})_3(\text{Ph}_3\text{P})[\text{CN}(\text{Me})\text{C}(\text{Me})\text{CHS}]$ . A limited number of oxidative addition reactions have been performed on (11) and (12). With tetrafluoroboric acid in acetic anhydride, the hydrido-metal tetrafluoroborate salts, e.g.  $[\text{OsH}(\text{CO})_4\text{L}]\text{BF}_4$ , are produced. With trimethyloxoniumtetrafluoroborate in  $\text{CH}_2\text{Cl}_2$ , (11) and (12) produced the osmium(II) complexes,  $[\text{OsMe}(\text{CO})_4\{\text{CN}(\text{Me})\text{C}(\text{Me})\text{CHS}\}]\text{BF}_4$  and  $[\text{OsMe}(\text{CO})_4\{\text{CN}(\text{Me}) \cdot \text{C}_6\text{H}_4 \cdot \text{S}\}]\text{BF}_4$  respectively.

$[\text{OsCl}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2]^+$  ( $\text{R} = p\text{-tolyl}$ ) reacts with  $\text{MeO}^-$  to give  $\text{OsCl}(\text{CO}_2\text{Me})(\text{CO})(\text{CNR})(\text{PPh}_3)_2$  [34], in which the methoxycarbonyl ligand bonds through the carbon atom. The starting material also reacts with  $\text{SH}^-$  with attack at the isocyanide ligand to give  $\text{Os}(\eta^2\text{-SCNR})(\text{CO})_2(\text{PPh}_3)_2$  in which the carbon and the sulphur atoms are bound to the metal.

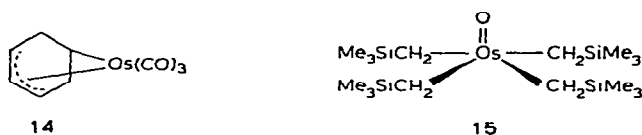
A small amount of the metallated complex  $\text{OsCl}_2(\text{P-C})\text{L}_2$ , ( $\text{P-C} = \text{PMe}_2\text{C}_{10}\text{H}_6$ ), is produced by the reaction of  $\text{OsO}_4$  with dimethyl(1-naphthyl)phosphine(L) in  $\text{HCl}/2\text{-methoxyethanol}$  solution [35]. The reaction between  $\text{OsO}_4$ , L and  $\text{HBr}$  gave only the metallated product  $\text{OsBr}_2(\text{P-C})\text{L}_2$ . In the presence of  $\text{NaOH}$  these complexes further metallate to give  $\text{Os}(\text{P-C})_2(\text{CO})\text{L}$ .

Reaction of  $\text{Os}_3(\text{CO})_{12}$  with azobenzene in refluxing octane gives a number of products [36], one of which has been characterised as (13), and which shows *cis* carbonyls and *cis*-Os-N bonds.



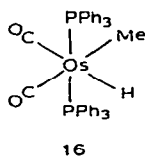
The reaction of osmium triphenylphosphine complexes  $\text{OsH}_4(\text{PPh}_3)_3$ ,  $\text{OsH}_2(\text{CO})(\text{PPh}_3)_3$  and  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  with triphenylphosphite in boiling decalin, yielded the *ortho*-metallated triphenylphosphite derivatives,  $\text{Os}(\text{P}-\text{C})_2(\text{PPh}_3)_2$  ultimately in all cases [37,38], but  $\text{OsCl}(\text{P}-\text{C})(\text{CO})(\text{PPh}_3)[\text{P}(\text{OPh})_3]$  was also isolated as an intermediate,  $[\text{P}-\text{C}=(\text{PhO})_2-\text{P}(\text{OC}_6\text{H}_4)]$ . Products are formed due to the stepwise insertion of  $\text{P}(\text{OPh})_3$  and loss of  $\text{PPh}_3$ , finally followed by *ortho*-metallation.

The reaction of tricarbonylcyclohexadienylosmium cation with sodium borohydride in water, yielded two products, one of which was identified by  $^1\text{H}$  NMR as the  $\sigma$ - $\eta$ -allyl derivative (14) [39].



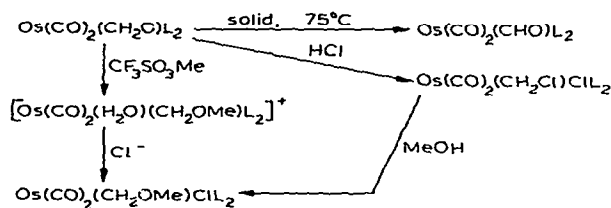
The reaction of three equivalents of  $(\text{Me}_3\text{SiCH}_2)_3\text{Mg}$  with  $\text{OsO}_4$  at  $-70^\circ\text{C}$  yields a dark red-brown solution from which  $\text{Os}(0)(\text{CH}_2\text{SiMe}_3)_4$  can be isolated as brown-yellow crystals that melt at room temperature [40]. A structure based on a square pyramid is inferred from  $^{13}\text{C}$  and  $^1\text{H}$  NMR data (15).

The complexes  $\text{Os}(\text{C}_6\text{H}_6)\text{L}_2$ ,  $[\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3]$  and  $\text{Os}(\text{C}_6\text{H}_6)\text{LL}'$ ,  $(\text{L} = \text{PMe}_3, \text{L}' = \text{C}_2\text{H}_4 \text{ and } \text{C}_3\text{H}_6)$ , have been prepared from the reduction of  $[\text{Os}(\text{C}_6\text{H}_6)\text{IL}_2]^+$  and  $[\text{Os}(\text{C}_6\text{H}_6)\text{ILL}']^+$  with  $\text{NaC}_{10}\text{H}_8$  in THF [41]. These osmium(0) complexes are strong Lewis bases and react with  $\text{MeI}$  to form stable cations containing  $\text{Os}-\text{Me}$  bonds,  $[\text{Os}(\text{C}_6\text{H}_6)\text{MeL}_2]^+$  and  $\text{Os}(\text{C}_6\text{H}_6)\text{-MeLL}'$ , which have been characterised by  $^1\text{H}$  NMR.



*Cis*-hydrido(methyl)dicarbonylbis(triphenylphosphine)osmium (16) has been prepared [42] by a series of transformations starting from the dihapto-formaldehyde complex,  $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2$  [43]. The dihapto complex can react further as shown in Scheme 1 [43], products being characterised by  $^1\text{H}$  NMR and IR spectroscopy.

The reaction of *mer*- $\text{OsCl}_3(\text{P}^n\text{Bu}_2\text{Ph})_3$  with the electron-rich olefin  $[\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})]_2$  yields *trans*- $\text{OsCl}_2[\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})]_4$  [44], with four mutually *trans* carbene ligands.  $[\text{Os}\{\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\}_4(\text{NO})]\text{Cl}$  [45] also has four *trans* carbene ligands, and is prepared as a very air and moisture sensitive compound from the reduction of



SCHEME 1

$\text{OsCl}_3(\text{NO})(\text{PPh}_3)_2$  by  $[\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})]_2^-$ .

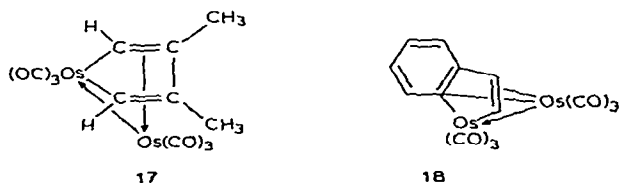
The dicationic complex  $[\text{Os}(\text{MeNC})_6](\text{FSO}_3)_2$  reacts with methylamine in water to give the bis-carbene complex  $\text{Os}(\text{CNMe})_4[\text{C}(\text{NHMe})_2]_2$  [46] in major yield, and the tris-carbene,  $\text{Os}(\text{CNMe})_3[\text{C}(\text{NHMe})_2]_3$  in minor yield.

In attempting to prepare  $\text{Os}(\text{CNBu}^t)_5$ ,  $[\text{OsCl}_2(1,5\text{-C}_8\text{H}_{12})]_n$  was reduced with potassium amalgam in the presence of excess  $\text{CNBu}^t$  [47]. The pale yellow product isolated was characterised as  $\text{Os}(1,5\text{-C}_8\text{H}_{12})(\text{CNBu}^t)_3$ .

### C. BINUCLEAR COMPLEXES

Relatively few binuclear complexes have been prepared; these have been mainly isolated by TLC and identified by spectroscopic methods.

The reaction of  $\text{Os}_3(\text{CO})_{12}$  with 2,3-dimethylbutadiene at  $200^\circ\text{C}$  for four days yields a product from which a small amount of a dimeric osmium complex,  $\text{Os}_2(\text{CO})_6\text{C}_6\text{H}_{10}$ , can be isolated [48]. This has been characterised by X-ray structural analysis [49], and was found to adopt the structure (17).



Cyclooctatetraene reacts with  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  to afford a complex mixture from which  $\text{Os}_2(\text{CO})_6(\text{C}_8\text{H}_6)$  can be isolated [50]; this has been shown by X-ray diffraction to have structure (18), in which one osmium has been incorporated into the original cyclooctatetraene ring to form a planar osmaindenyl system, with osmium to carbon bond lengths of ca.  $2.08 \text{ \AA}$ .

The dinuclear complex  $\text{HOs}(\text{CO})_4\text{Os}(\text{CO})_4\text{CH}_3$  is obtained on the decomposition of *cis*- $\text{OsH}(\text{CO})_4(\text{CH}_3)$ , in the absence of air and light [13,51]. This product can further react with  $\text{CCl}_4$  to produce  $\text{ClOs}(\text{CO})_4\text{Os}(\text{CO})_4\text{CH}_3$ , or can decompose to yield a moderately stable white solid which has been characterised as  $\text{CH}_3(\text{OC})_4\text{OsOs}(\text{CO})_4\text{Os}(\text{CO})_4\text{CH}_3$  [12]. Ethylene will also react with  $\text{HOs}(\text{CO})_4\text{Os}(\text{CO})_4\text{CH}_3$  (at 1 atm. and  $75^\circ\text{C}$  in heptane) to produce the dinuclear mixed dialkyl  $\text{C}_2\text{H}_5\text{Os}(\text{CO})_4\text{Os}(\text{CO})_4\text{CH}_3$  [13].

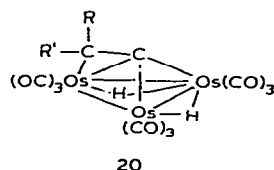
Upon reacting  $\text{Os}_3(\text{CO})_{12}$  with  $\text{Pt}(\text{PPh}_3)_2(\text{stilbene})$  in refluxing toluene, three minor products can be isolated. One of these has been characterised spectroscopically and by mass spectrometry as the *ortho*-metallated complex,  $\text{Os}_2(\text{CO})_6[\text{P}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2$  [52].

#### D. TRI-NUCLEAR OSMIUM COMPLEXES

Osmium cluster compounds have gained importance in that they are alleged to provide models for modes of coordination of organic groups onto metal surfaces.

The thermolysis of  $\text{Os}_3(\text{CO})_{12}(\text{CH}_3)_2$  (**19**) has been shown [53] to yield  $\text{Os}_3(\text{CO})_{12}$  and methane—the methane being produced by methyl radical formation followed by attack on the solvent, (confirmed by the use of deuterated solvents and analysis of the products produced). At room temperature excess hydrogen bromide rapidly reacts with (**19**), to cleave both methyl groups and produce  $\text{Os}_3(\text{CO})_{12}\text{Br}_2$ ; with one mole of each reactant, the partial cleavage product  $\text{Os}_3(\text{CO})_{12}\text{Br}(\text{CH}_3)$  can be isolated.

The reaction of alkenes ( $\text{RR}'\text{CCH}_2$ ), ( $\text{R} = \text{R}' = \text{H}$ ;  $\text{R}, \text{R}' = \text{H}$  or alkyl, etc.), with  $\text{Os}_3(\text{CO})_{12}$  produces  $\text{Os}_3\text{H}_2(\text{CCRR}')(\text{CO})_9$  which is believed to have structure (**20**) [54–56] in which there is a direct  $\text{Os}-\text{CRR}'$  bond. The complex ( $\text{R} = \text{R}' = \text{H}$ ) can be hydrogenated to the ethylidyne compound  $\text{Os}_3\text{H}_3(\text{CCH}_3)(\text{CO})_9$  by refluxing in *n*-heptane under hydrogen.



$\text{Os}_3(\text{CO})_{12}$  reacts with a number of alkynes (e.g., acetylene, 2-butyne, 3-hexyne, etc.) to give a variety of complexes [57] that either:

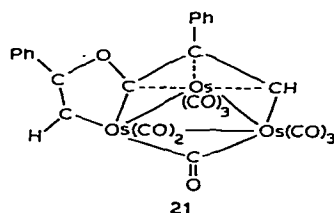
(a) result from the substitution of carbonyl groups with intact ligand molecules (e.g.,  $\text{Os}_3(\text{CO})_{10}\text{L}$ ). In these, the ligand generally  $\sigma$ -bonds to two osmium atoms and  $\pi$ -bonds to the third.

(b) result from the coordination of ligands on metal centres followed by the formation of osmium cyclopentadiene units, e.g.,  $\text{Os}_3(\text{CO})_9\text{L}_2$  [58], also containing  $\text{Os}-\text{C}$  bonds.

(c) result from the activation of hydrogen atoms to yield  $\text{Os}_3\text{H}(\text{CO})_9(\text{L}-\text{H})$ .

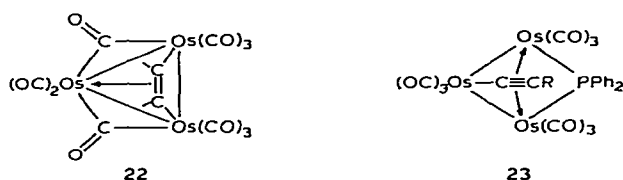
Phenylacetylene reacts with  $\text{Os}_3(\text{CO})_{12}$  to produce a mixture of products: one of these,  $\text{Os}_3(\text{CO})_9(\text{HC}_2\text{PhCOCPhCH})$  (**21**) [59] results from two phenylacetylene molecules linking through a carbon and oxygen derived from a carbonyl group. The bond order in the rings has not been elucidated.



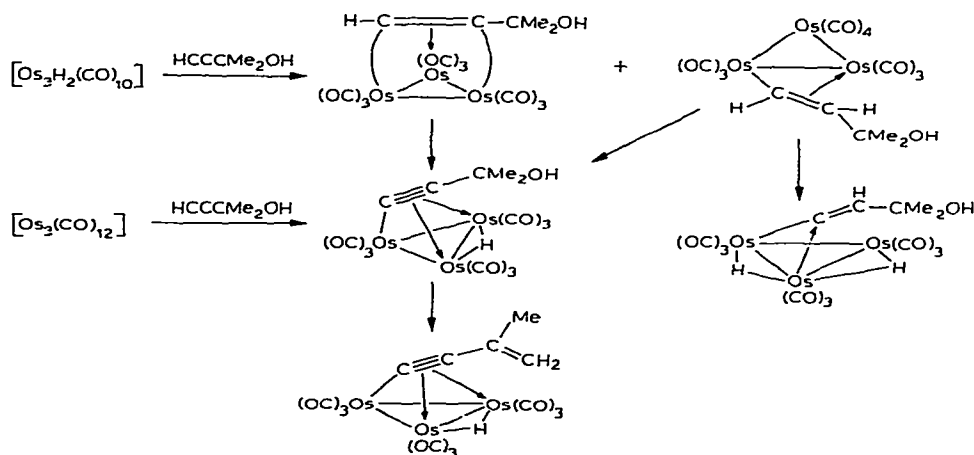


Another product (**22**) [60] reacts with excess ligand to ultimately yield 1,2,4-triphenylbenzene.

The reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{Ph}_2\text{PC}\equiv\text{CR}$  ( $\text{R} = i\text{-Pr}$  or  $t\text{-Bu}$ ) in heptane at  $75^\circ\text{C}$  for 4 h in the presence of  $\text{Me}_3\text{NO}$  produces yellow  $\text{Os}_3(\text{CO})_{11}(\text{Ph}_2\text{PC}\equiv\text{CR})$  [61]. Treatment of this in decalin for 5 h yields the product  $\text{Os}_3(\text{CO})_9(\text{C}\equiv\text{CR})(\text{PPh}_2)$  (**23**).



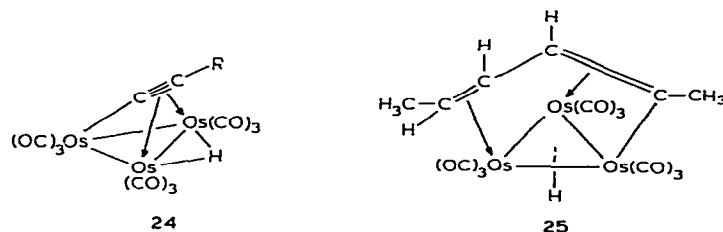
$\text{Os}_3\text{H}_2(\text{CO})_{10}$  and  $\text{Os}_3(\text{CO})_{12}$  react with 3-hydroxy-3-methylbut-1-yne to give a variety of products, Scheme 2 [62]. Structures are proposed on the basis of  $^1\text{H}$  NMR data. Dynamic NMR studies on these compounds have allowed the different modes of ligand coordination to be observed.



SCHEME 2

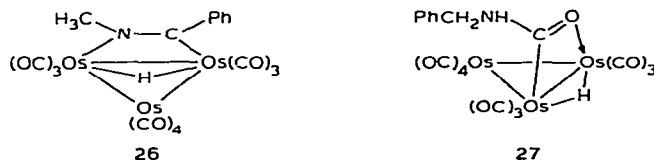
Complexes of type (**24**) [63] are produced on refluxing  $\text{Os}_3(\text{CO})_{12}$  with  $\text{HOCMe}_2\text{C}\equiv\text{CCMe}_2\text{OH}$ , or  $\text{HOCPh}_2\text{C}\equiv\text{CPh}_2\text{OH}$  at  $130^\circ\text{C}$  in yields of up to 70%.

With dienes,  $\text{Os}_3(\text{CO})_{12}$  produces a complex in which the diene ligand

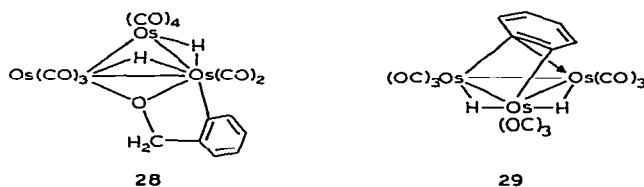


$\sigma$ -bonds to one of the osmium atoms and  $\pi$ -bonds to the other two [64], e.g. for  $\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_9)$  (**25**).

The compound  $\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_6\text{H}_5\text{CNCH}_3)$  (**26**) has been shown by X-ray diffraction [65] to have the structure indicated, in which one carbon atom is coordinated to an osmium centre, and the nitrogen coordinated to a second osmium.



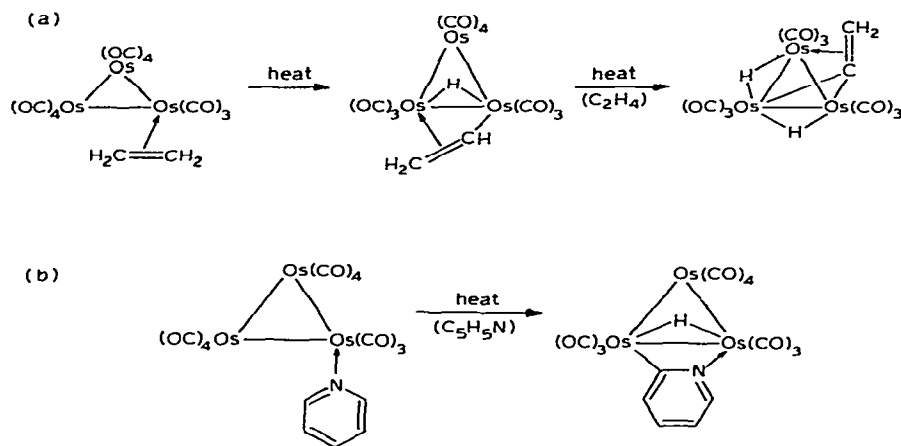
The reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{N}(\text{CH}_2\text{Ph})\text{H}_2$  yields  $\text{Os}_3\text{H}(\text{CO})_{10}[\text{OCN}(\text{CH}_2\text{Ph})\text{H}]$  (**27**) [66]; better yields are obtained if the reaction is performed under a carbon monoxide atmosphere. On repeating the reaction with benzyl alcohol only  $\text{Os}_3\text{H}(\text{CO})_{10}(\text{OCH}_2\text{Ph})$  is produced. Thermolysis of this product in refluxing nonane yields two products, isolated and characterised as (**28**) and (**29**).



Trimethylamine and *N,N*-dimethylbenzylamine react with  $\text{Os}_3(\text{CO})_{12}$  by elimination of alkane or  $\text{H}_2$  to give the compounds  $\text{Os}_3\text{H}(\text{CO})_{10}(\mu^2\text{-RC}=\text{NMe})$ , ( $\text{R} = \text{H}$  or  $\text{Ph}$ );  $\text{Os}_3\text{H}(\text{CO})_{10}(\mu^2\text{-C}=\text{NMeR})$ , ( $\text{R} = \text{Me}$  or  $\text{PhCH}_2$ ); and  $\text{Os}_3\text{H}(\text{CO})_9(\mu^3\text{-HC}=\text{NMe})$  [67]. In all the compounds prepared, *ortho*-metallation and the formation of unsaturated ligands dominate this chemistry.

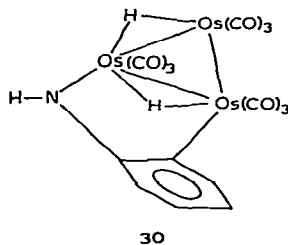
$\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ , prepared from the reaction of  $\text{Os}_3(\text{CO})_{12}$  with trimethylamine oxide in methanol, reacts with ethylene or pyridine to produce  $\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{H}_4)$  and  $\text{Os}_3(\text{CO})_{11}(\text{C}_5\text{H}_5\text{N})$  respectively [68]; which when

heated in *n*-octane, produce the osmium–carbon bonded complexes  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{CCH}_2)$  and  $\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_5\text{H}_4\text{N})$  as shown in Scheme 3. Other pyridine complexes prepared include [69]:  $\text{Os}_3\text{H}(\text{CO})_9(\text{NC}_5\text{H}_4)(\text{py})$  (2 isomers),  $\text{Os}_3\text{H}_2(\text{CO})_8(\text{NC}_5\text{H}_4)$ , and  $\text{Os}_2(\text{CO})_6(\text{NC}_5\text{H}_4)$  (2 isomers), in which *ortho*-metallation occurs between two adjacent osmium atoms forming four-membered Os–Os–C–P rings.



SCHEME 3

Aniline reacts with  $\text{Os}_3(\text{CO})_{12}$  (reflux, 1 h) to yield the product  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{HNC}_6\text{H}_4)$  [70]. This compound, (30), contains the *ortho*-metallated aniline ligand, which has been characterised by IR and NMR. A similar product is obtained on using *para*-fluoroaniline; however *p*-toluidine shows no evidence of *ortho*-metallation.



Complexes of stoichiometry  $\text{Os}(\text{CO})_2(\text{Bq})_2$  ( $\text{Bq}$  = benzo-[h]-quinoline) result from the reaction of  $\text{Os}_3(\text{CO})_{12}$  with benzo[h]quinoline [71]. Infrared study shows that the carbonyls are *cis* and that there are two *ortho*-metallated ligands; however the overall configuration has not been determined. The reaction was not complete even after 230 h reflux.

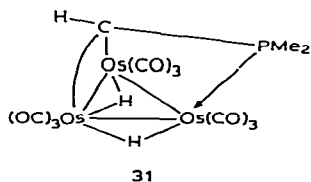
A range of trinuclear osmium complexes has been prepared from the oxidative addition of aldehydes with  $\text{Os}_3(\text{CO})_{12}$  [72]. Most of the acyl

complexes prepared were found to decarbonylate to give products containing coordinated formyl groups,  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{R}'\text{CCHO})$ . Analogous species were obtained from cyclohexanone and  $\text{Os}_3(\text{CO})_{12}$  or from cyclohexenone and  $\text{Os}_3\text{H}_2(\text{CO})_{10}$ .

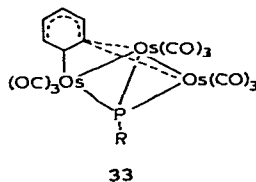
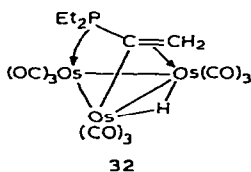
Reaction of  $\text{Os}_3(\text{CO})_{12}$  with triphenylphosphine in the ratio 1:2 leads to a complex mixture of products [73]; of interest are the *ortho*-metallated complexes:  $\text{Os}_3\text{H}(\text{CO})_9(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$  [74],  $\text{Os}_3\text{H}(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$  [75],  $\text{Os}_3\text{H}(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$  [75],  $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$  [74].

$\text{LiBH}(\text{C}_2\text{H}_5)_3$  reacts with  $\text{Os}_3(\text{CO})_{12}$  in tetrahydrofuran at  $-30^\circ\text{C}$  to form a deep red solution [76].  $[\text{Os}_3(\text{CO})_{11}\text{CHO}]^-$  has been detected spectroscopically ( $^1\text{H}$  NMR) in solution. Upon warming to  $0^\circ\text{C}$ , the formyl signals disappear and signals due to hydride complexes build up; these are possibly due to  $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$ ,  $[\text{Os}_4\text{H}_2(\text{CO})_{12}]^{2-}$  or  $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ .

On heating  $\text{Os}_3(\text{CO})_{11}(\text{PMe}_3)$  in refluxing nonane for several hours a complex  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{Me}_2\text{PCH})$  (**31**) [77] is formed in which the basic interaction between the  $\text{Me}_2\text{PCH}$  group and the metal atoms is a  $\sigma$ -metal to carbon bond to two osmium atoms.



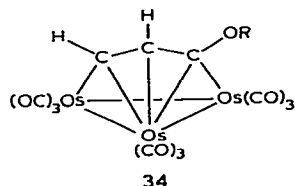
$\text{Os}_3(\text{CO})_{11}(\text{PEt}_3)$  has been converted [78] to the alkene compound  $\text{Os}_3\text{H}(\text{CO})_9(\text{Et}_2\text{PC}=\text{CH}_2)$  (**32**), and then by isomerisation to the alkyne compound  $\text{Os}_3\text{H}(\text{CO})_9(\text{PEt}_2)(\text{HCCH})$ .



Thermolysis of the compounds  $\text{Os}_3(\text{CO})_{11}\text{PPh}_2\text{R}$ , ( $\text{R} = \text{Me, Et, Ph}$ ), produces  $\text{Os}_3(\text{CO})_9(\text{PR})(\text{C}_6\text{H}_4)$  (**33**) which has been shown [79] by X-ray crystallography to have a benzyne ligand containing an osmium to carbon  $\sigma$ -bond.

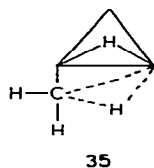
Acetylene (moist), methylacetylene or phenylacetylene reacts with  $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$  to yield as its major product  $\text{Os}_3(\text{CO})_9(\text{C}_3\text{H}_2\text{OR})\text{H}$ , ( $\text{R} = \text{H, CH}_3$  or  $\text{C}_6\text{H}_5$ ), (**34**) [80]. The allyl-methylether derivative

$\text{Os}_3(\text{CO})_9(\text{C}_3\text{H}_2\text{OCH}_3)\text{H}$  is prepared by the reaction of an allyl-alcohol product with NaH and MeI in tetrahydrofuran.

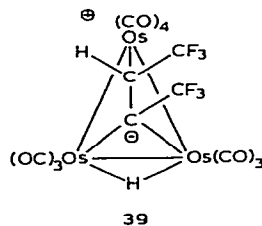
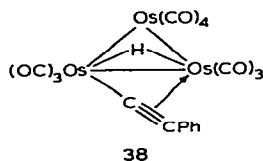
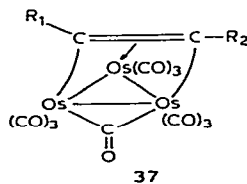
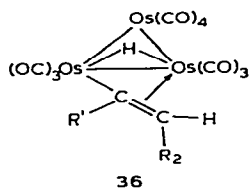


The crystal structure of  $\text{Os}_3\text{H}_2(\text{CO})_{10}\text{CH}_2$  shows the presence of a bridging methylene carbon 2.15 Å from two edge osmium atoms [81]. Neutron diffraction and solution  $^1\text{H}$  NMR studies have shown the presence of an equilibrium isotope effect which favours the incorporation of deuterium into the methylene group.

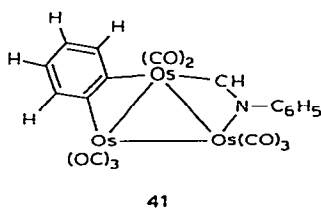
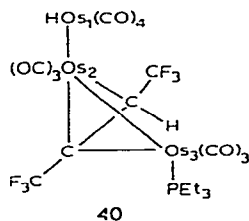
The cluster compound  $\text{Os}_3\text{H}(\text{CO})_{10}\text{CH}_3$  has been shown by  $^1\text{H}$  NMR spectroscopy on partially deuterated samples, to consist of a distorted  $\sigma$ -bonded methyl group which interacts ( $\text{C}-\text{H} \cdots \text{Os}$ ) with a second osmium atom (35) [82]. In solution, tautomerisation occurs [83]; this has been directly observed, and shown to be solvent dependent.



Reaction of  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  with acetylene [84] or but-1-yne [85], produces a complex containing the bridging vinyl group (36) [86–88]; with propyne a mixture of (36) and (37) is formed [84], whilst on reaction with phenylacetylene (38) [84] is produced.

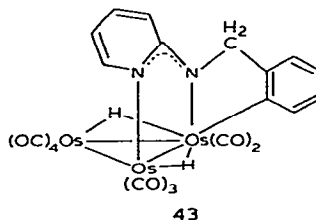
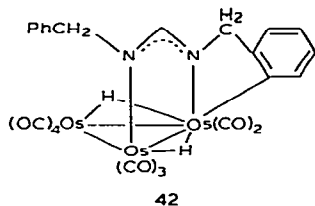


Upon reacting  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  with  $\text{F}_3\text{CCCCF}_3$  in hexane at room temperature, a complex is produced in which the organic fragment is bound to all three osmium atoms (**39**) [89]. Further reaction with  $\text{PEt}_3$  leads to the formation of  $\text{Os}_3\text{H}(\text{CO})_{10}(\text{PEt}_3)(\text{CF}_3\text{CCHCF}_3)$  (**40**) as the major product (30%) [90]. The vinylic ligand  $\sigma$ -bonds to  $\text{Os}_1$  and  $\pi$ -bonds to  $\text{Os}_2$ . This reaction is formally regarded as a reduction reaction in that two electrons are added to the cluster.



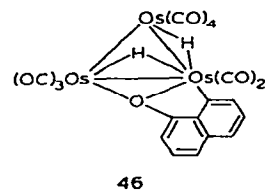
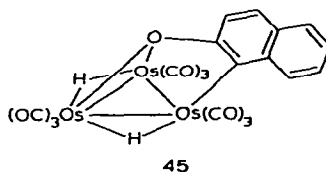
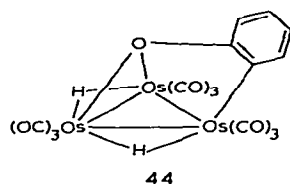
The product of the reaction of  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  with  $\text{CNC}_6\text{H}_5$  has been pyrolysed to produce  $\text{Os}_3\text{H}_3(\text{CO})_8(\text{C}_6\text{H}_4)(\text{HC}=\text{NC}_6\text{H}_5)$  (**41**) [91]. Structural and  $^1\text{H}$  NMR analysis has allowed the structure to be elucidated; the benzyne and formimidoyl ligands bridge opposite faces of the osmium triangle.

Treatment of  $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$  with  $\text{PhCH}_2\text{N}=\text{CHNHCH}_2\text{Ph}$  in a mixture of  $\text{C}_8\text{H}_{14}$  and chloroform, and subsequent thermolysis at  $125^\circ\text{C}$  yields (**42**) [92] in which an *ortho*-metallated cluster is formed. On using *N*-benzyl-2-aminopyridine, (**43**) is produced. Both these compounds were isolated by TLC and characterised spectroscopically.

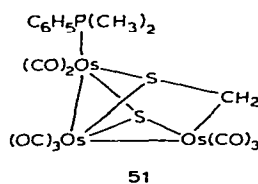
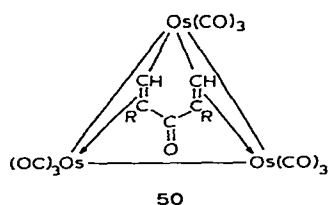
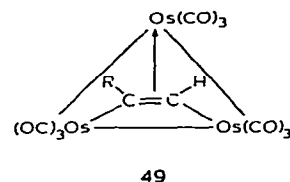
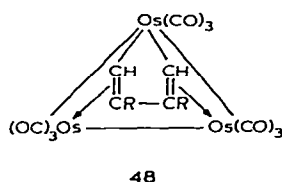
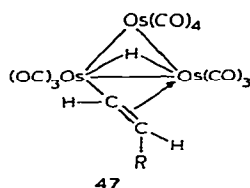


$\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$  reacts with  $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$  in refluxing hexane to produce  $\text{Os}_3(\mu\text{-H})(\text{CO})_{12}(\mu\text{-}\eta^2\text{-C}_6\text{H}_5\text{C}=\text{NCH}_3)$  and  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9[\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4]$ , the latter product containing an *ortho*-metallated phenyl ring [93].

$\text{Os}_3\text{H}(\text{CO})_{10}(\text{OR})$ , ( $\text{R}$  = alkyl, aryl, etc.), compounds have been prepared from the reaction of  $\text{OsO}_4$  and carbon monoxide in a suitable solvent ( $\text{HOR}$ ) [94]. If  $\text{R}$  = aryl these compounds can *ortho*-metallate upon refluxing in nonane to produce, e.g.  $\text{R}$  = Ph, (**44**). If  $\text{R}$  = 2-naphthyl then two isomers are obtained, (**45**) and (**46**).

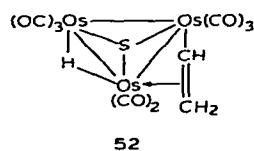


Cyclohexadiene reacts with  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  under moderate conditions to give  $\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_8)$  [95]. Cyclohexadiene is a very good leaving group and so the compound readily reacts with ethylenes and acetylenes to give a variety of triangulo-cluster compounds, e.g. (47)–(50).

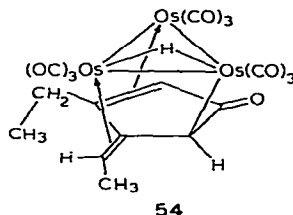
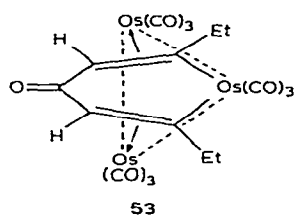


The reaction of  $\text{Os}_3\text{H}_2(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$  with carbon disulphide leads to the formation of  $\text{Os}_3(\text{CO})_9(\text{SCH}_2)(\mu_3\text{-S})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ , which when refluxed in hexane, loses one mole of carbon monoxide to form the complex  $\text{Os}_3(\text{CO})_8(\text{SCH}_2)(\mu_3\text{-S})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$  (51) [96] in which the  $\text{SCH}_2$  carbon is  $\sigma$ -bonded to one osmium atom, and the sulphur atom bridges the other two.

The high reactivity of  $\text{Os}_3\text{H}(\text{CO})_9(\text{SR})$ , ( $\text{R} = \text{Me}$ , or  $\text{Et}$ ), associated with the variable coordination of the sulphur ligand, has been utilised in the preparation of a range of adducts [97], including the first example of an ethylene molecule  $\pi$ -bonded to a single metal centre,  $\text{Os}_3(\text{CO})_9(\text{C}_2\text{H}_4)(\text{SR})$ . On heating this in *n*-octane under ethylene,  $\text{Os}_3\text{H}(\text{CO})_8(\text{CH}:\text{CH}_2)\text{S}$  is produced (52) in which the  $\pi$ -bonded ethylene ligand has been converted to a vinyl ligand.

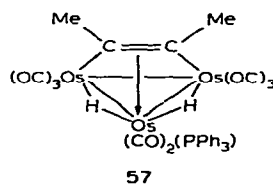
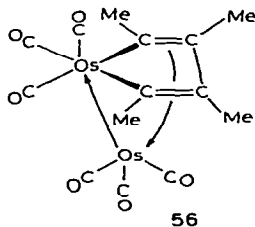
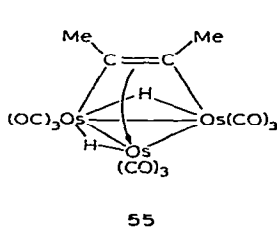


Pyrolysis of the osmiacyclohexadieneone complex (**53**) under drastic conditions yields the product  $\text{Os}_3\text{H}(\text{CO})_9[\text{CHC}(=\text{O})\text{CH}=\text{CEtC}(=\text{CHMe})]$  (**54**) [98–100]. X-ray structural analysis has shown that the organic part of the molecule contains an Os—C  $\sigma$ -bond to one osmium atom and  $\pi$ -interactions to the other two atoms.



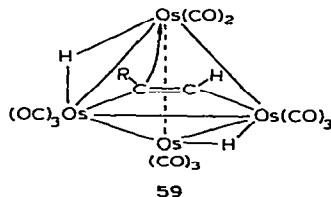
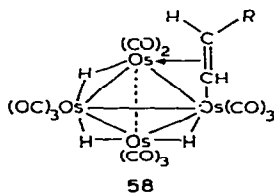
Halomethylidyne clusters have been prepared [101] from the reaction of  $\text{Os}_3\text{H}_3(\text{CO})_9(\mu_3\text{-COCH}_3)$  with borontrihalide, as  $\text{Os}_3\text{H}_3(\text{CO})_9(\text{CX})$ .

The reaction of  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)$  [102] with excess dimethylacetylene in hexane at 60°C for 4 days led to a mixture of products which were separated by chromatography and sublimation techniques, and characterised by mass spectrometry, NMR and IR. Of interest are the products (**55**)–(**57**).



#### E. TETRANUCLEAR OSMIUM COMPLEXES

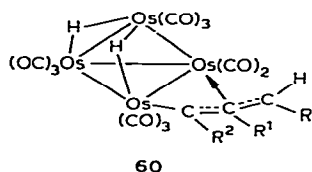
The irradiation of  $\text{Os}_4\text{H}_4(\text{CO})_{12}$  in benzene [103] provides a source of unsaturated species such as “ $\text{Os}_4\text{H}_2(\text{CO})_{12}$ ” and “ $\text{Os}_4(\text{CO})_{12}$ ”. In the presence of alkenes,  $\text{RCHCH}_2$  ( $\text{R} = \text{H}, \text{Ph}$  [104] or  $t\text{-Bu}$ ), or  $\text{cis-CHPh=CHPh}$ ,  $\text{Os}_4\text{H}_3(\text{CO})_{11}(\text{HC}_2\text{HR})$  (**58**) can be isolated by TLC. On heating this compound in boiling octane, or on the reaction of  $\text{Os}_4\text{H}_4(\text{CO})_{12}$  with alkene in boiling toluene for 5 days, dehydrogenation occurs and  $\text{Os}_4\text{H}_2(\text{CO})_{11}(\text{HC}_2\text{R})$  (**59**) is obtained. This dehydrogenation is not reversible. Molecular formulae





were determined by mass spectrometry and  $^1\text{H}$  NMR. Similar products to (58) are obtained by the reaction of  $\text{Os}_4\text{H}_4(\text{CO})_{12}$  with cycloolefins (cyclooctatetraene, cycloocta-1,5-diene, cyclohexene and norbornene) [105]. X-ray analysis shows the similarity in structure with the ring  $\sigma$ -bonded to one metal atom and  $\pi$ -bonded to another.

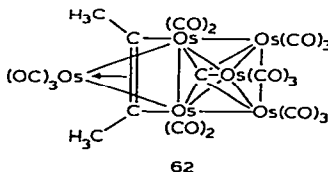
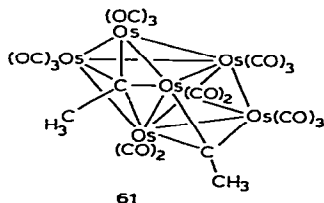
The reaction of carbon monoxide with  $\text{Os}_4\text{H}_3(\text{CO})_{11}(\text{CR}^1=\text{CHR}^2)$ , ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{Ph}$ ;  $\text{R}^1 = \text{R}^2 = \text{Ph}$ ), at high temperatures and pressures produces  $\text{Os}_4\text{H}_2(\text{CO})_{12}(\text{HCCH}_2\text{Ph})$  in which the methylene carbon bridges a short edge of a distorted tetrahedra of osmium atoms [106]. Acetylenes ( $\text{C}_2\text{H}_2$ ,  $\text{HCCPh}$  and  $\text{PhCCPh}$ ) react with  $\text{Os}_4\text{H}_3(\text{CO})_{11}(\text{CH}=\text{CH}_2)$  to give addition products, in 50% yield, in which a  $\pi$ -allylic bond is formed between the organic fragment and one of the osmium atoms (60).



The high pressure reaction of ethylene with  $\text{Os}_3(\text{CO})_{12}$  in hexane yields the complexes  $\text{Os}_3\text{H}_2(\text{CO})_9 \cdot \text{CCH}_2$ ,  $\text{Os}_4(\text{CO})_{12}\text{CH}:\text{CH}$  and  $\text{Os}_4(\text{CO})_{12}(\text{HC}=\text{CEt})$  [107]. These have been characterised by X-ray crystallography. In both  $\text{Os}_4$  complexes the metal atoms adopt the “butterfly” configuration in which the acetylenic ligands lie over the “butterfly” with the organic C–C bond parallel to the Os–Os “hinge” bond. The acetylenic ligand is  $\pi$ -bound to the two “wing-tip” metal atoms, and  $\sigma$ -bound to the “hinge” atoms.

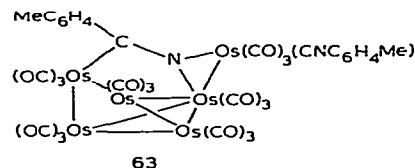
#### F. HEXANUCLEAR OSMIUM COMPLEXES

The reaction of  $\text{Os}_6(\text{CO})_{18}$  with ethylene yields two products,  $\text{Os}_6(\text{CO})_{16}(\text{CMe}_2)$  (61), and  $\text{Os}_6(\text{CO})_{16}(\text{MeC}=\text{CMe})\text{C}$  (62) [108]. In (61) the  $\text{CCH}_3$  moiety is formulated as a 3-electron donor ligand, whilst in (62) the but-2-yne ligand is  $\pi$ -bonded to one osmium atom and  $\sigma$ -bonded to another two.



The structure of the isocyanide substituted hexaosmium cluster  $\text{Os}_6(\text{CO})_{18}(\text{CNC}_6\text{H}_4\text{Me})_2$  (63) [109] has been determined and has shown that

both the carbon and the nitrogen atoms of one of the isocyanide moieties bond, via single bonds, to the osmium framework.



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